Evaluation of PCM activation using changes in physical properties during phase transition for visualization of passive building envelope technologies

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ABSTRACT
There is a large potential to use passive technologies for increasing the thermal comfort and reducing the energy use for heating and cooling in buildings. In many cases the occupants of the building lack good practical understanding and knowledge on how these passive technologies function. Therefore, there is a challenge to utilize their full potential. For instance, the potential energy savings for space heating and cooling is 5-21 % with phase change materials (PCMs) integrated in building envelopes (e.g. encapsulated in the plaster board). Consequently, there is a pedagogical problem to explain how and when PCMs are active in regard to passive adjustment to changes in the indoor environment. The reason for this is the lack of proper tools. Temperature sensors alone or numbers on the energy use is not enough to give the occupants information on how to use the passive technologies in the most efficient way. One aim of this study is therefore to explore properties that can be used as a foundation for the development of technologies for visualizing the phase transition. Laboratory experiments are used to evaluate three methodologies based on density, viscosity and optical properties that change when a PCM undergoes a phase transition. The results are compared to phase transition measurements by DSC. The methods are tested on a type of organic PCMs, polyethylene glycol (PEG), of different molecular weights. From the results it is obvious that all three methods can be used to differentiate the phases even if there remains challenges before practical implementation in buildings is possible.

KEYWORDS
Laboratory study, PCM, DSC, density, viscosity, light transmittance

INTRODUCTION
All energy use in society causes emissions of greenhouse gases. Around 40 % of the energy use in the developed countries is used for heating and cooling in buildings, which leads to a large contribution to the total greenhouse gas emissions from this sector (IEA, 2013). There is a variation of the heating power demand in buildings over the year and between the hours of the day. This creates a mismatch between the peak heating and cooling power demand of buildings and the availability of renewable energy sources. By using technologies that reduces the variations in indoor temperature in buildings, the size of the heating system can be reduced and renewable energy sources can be utilized. One such technology is phase change materials (PCMs). In these materials energy is either absorbed or released during the phase transition, which for a building application should take place around room temperature.

In contrast to conventional sensible energy storage materials such as masonry, rock or water, PCMs are able to store 5-14 times as much energy per unit volume. This is due to the latent heat (LH) storage potential that occurs during isothermal phase transitions (Jeon et al., 2012). It has previous been shown that it is possible to save 5-20 % of the total annual energy required for heating and cooling of a building if PCMs are integrated in the building envelope

(Kalagasidis, 2014). But if e.g. windows are opened at an elevated temperature in the building, this excess heat is lost. Therefore the occupants have to be educated and aware of the passive technology and, most importantly, when it is activated.

Technologies for visualizing the PCM activation process can increase the understanding and knowledge among occupants. Jin et al. (2014) concluded that the performance of PCM is affected by its state of phase transition. The best performance was found for the PCMs which was partially melted. Then it would release the latent heat quickly for best performance. Temperature sensors alone or numbers on the energy use is not enough to give the occupants information on how to use the passive technologies in the most efficient way. It is therefore a pedagogical problem to explain how and when PCMs are active in regard to passive adjustment to changes in the indoor environment. The reason for this is the lack of proper tools and new and innovative analytical techniques and solutions to visualize the phase transition are therefore needed.

There are many different types of commercially available PCMs, each with its own specific properties when it comes to heat storage capacity, phase transition temperature intervals, degree of supercooling, crystalline structure and other physical- and chemical properties (Kalnæs and Jelle, 2015). The standard measurement procedures used today are not sufficient to completely characterize a PCM (Mehling et al., 2006). Since all types of PCMs changes in different physical properties during the phase transitions and as a consequence, the optimal characterization technique will not be the same. A previous study tested the PCM on salt hydrates using the TPS method (Johansson et al., 2015) and it was proved to be an appropriate method to differentiate between solid and liquid PCM. However, several limitations regarding sample preparation and temperature stabilization remains unsolved. Steinmaurer et al. (2014) tested two other methods based on the volumetric change of PCMs and damping properties during the phase transition. They found that paraffins, with a large density difference between the solid and the liquid phase could be measured with the first method while the second method could be applicable for all types of PCMs. The effective properties of the PCMs may change when the PCM is encapsulated and installed in the building envelope since they are no longer in their pure form as tested in the laboratory (Kalnæs and Jelle, 2015). Therefore, one aim of this study is to explore different measurement techniques to find the most appropriate performance indicator for PCMs made of PEG. This is done by evaluating three measurement methods to detect changes in density, viscosity and light transmittance. Of particular interest is to find cheap and reliable measurements techniques to visualize the phase transition, i.e. to distinguish between the solid and liquid states of the material.

METHODS

In this study the organic PCM polyethylene glycol (PEG) of different molecular weights (600, 1000, 1500, 4000 or 6000 g/mol) were analyzed with respect to various physical properties. All chemicals were laboratory graded and provided by Fisher Scientific®. It should be noted that PEG is a polymer and that the molecular weight is related to the length of the polymer chain. In addition, the melting point for a polymer is not a real solid to liquid phase transition but a rather a transition from a crystalline or semi-crystalline solid phase to a liquid like amorphous state. For the latter, the notation ‘liquid like’ is therefore used in the following.

Calorimetric measurements using DSC

A common method for thermal analysis of PCMs is differential scanning calorimetry (DSC). This method measures the amount of heat absorbed or released by a material during temperature changes. A small, preferably homogeneous sample, is placed inside a

hermetically sealed pan and put into a furnace chamber within the DSC apparatus. Next to the pan containing the sample an identical empty pan is placed, in a similar position, for the use as a reference. The temperature development and thermal resistance of the material is measured using temperature sensors during heating and/or cooling and compared to that of the reference. This makes it possible to accurately measure the heat flow. The deviation between the sample and reference temperature is measured and used to evaluate the PCM. . In this study the DSC measurements (DSC 1, Mettler Toledo®) is used as reference for the other tested measurement techniques. Solid materials in the range of 10-30 mg were heated above their melting point and then cooled again below their solidification point. The temperature change rate was set to 0.1 K/min. The average results from 3 thermal cycles was calculated. The phase transition temperatures determined by the DSC measurements were then used as references for the measurements on various physical properties (described below).

Density measurements

A small liquid sample of approximately 1 ml PCM was injected into an oscillating U-tube sensor in an Anton-Paar density meter (DMA 4500M®). The density is determined with great accuracy, including correction of the viscosity influence. The instrument electronically excites the U-tube sensor to simultaneously oscillate at the fundamental resonant frequency and its harmonics. The oscillation characteristics are measured with an integrated reference oscillator providing the pace. The reference oscillator is positioned in close thermal contact with the oscillating U-tube. This positioning enables the reference oscillator to compensate for all drifts arising from temperature stress. Measurements were taken every 0.5 °C, starting at a temperature where the PCM was completely in its liquid like state and then cooled until it was completely solidified.

Viscosity measurements

The viscosity measurements were performed using a rheometer from Bohlin Instruments (CVO 200®) equipped with a cooling/heating system. About 100 ml material was added in a cup at a temperature above the melting point of the PCM. The rotor was equipped with a bob and submerged into the material. The rotation speed was set to a constant shear rate during the test cycle. The sample was inserted in its liquid like state and the material was cooled down below the solidification temperature. Then it was heated up again to the liquid like state while continuously measuring the shear stress during the test cycle.

Light transmittance measurements

The light transmittance of the PCMs was measured using an in-house constructed setup with a light source, lens and light sensor, see Figure 1. The setup made it possible to measure the amount of light transmitted through a material during solidification. The light source was a white 1.5 W LED lamp 230-240 V and 50 Hz focused by a lens to hit the center of a cuvette filled with 3.5 ml of the PCM. Behind the cuvette, a light sensor (HAGNER® EC1) was placed to measure the intensity of the light transmitted through the material. These experiments were performed in a dark room at 21 °C. The material was heated and placed in the cuvette where it was cooled by the ambient air with approximately 1 °C/min. The temperature of the surface of the sample was monitored by using infrared thermography (FLIR b50). The temperature and the transparency were logged every 20 seconds during the measurements.

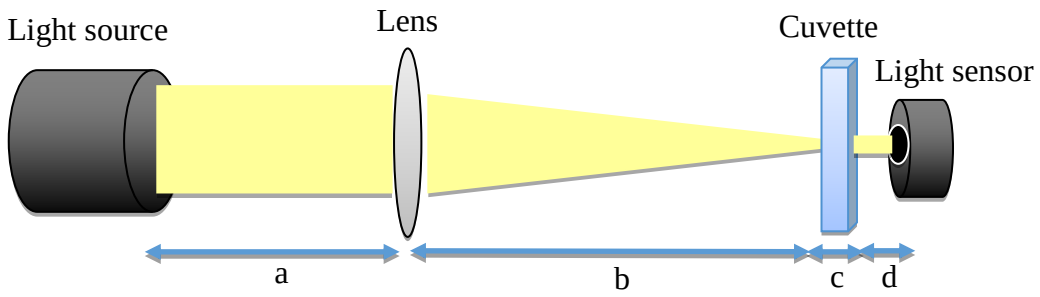

Figure 1. Set up for the light transmittance measurements with light source, lens, sample holder and light sensor. The length of a = 40 cm, b = 94 cm, c = 1 cm and d = 0.5 cm (Paberit and Öjerborn, 2016).

RESULTS

As described above, in this study the three physical properties viscosity, density and light transmittance were investigated as a function of temperature in order to correlate these to the phase transition temperatures measured by DSC for each of the tested PEGs. The results for the PEG600 and PEG1000 are presented for the viscosity and density measurements while the PEG1000, PEG1500, PEG4000 and PEG6000 are tested using the optical setup.

Viscosity Measurement Results

The results obtained by DSC and the viscosity changes during heating and cooling are presented in Figure 2 for PEG600 (A and C) and PEG1000 (B and D). It can be observed that on heating (A and B), i.e. when the material absorb heat and undergo a phase transition from a solid to a liquid like state, the onset temperature of the viscosity is in good agreement with the first peak maximum obtained in the DSC scan. Consequently, at the same time as the material becomes fluid there is a substantial change in viscosity. Meanwhile, on cooling (C and D) the change in viscosity occurs at the same temperature as the DSC curve deviates from the baseline, i.e. at the temperature when the material starts to solidify. Worth noting is that there also is a drop in the viscosity on cooling at lower temperatures despite that the viscosity is expected be infinite when a material becomes solid. The reason for this is that it is not possible to perform any measurements in the solid state with this type of instruments.

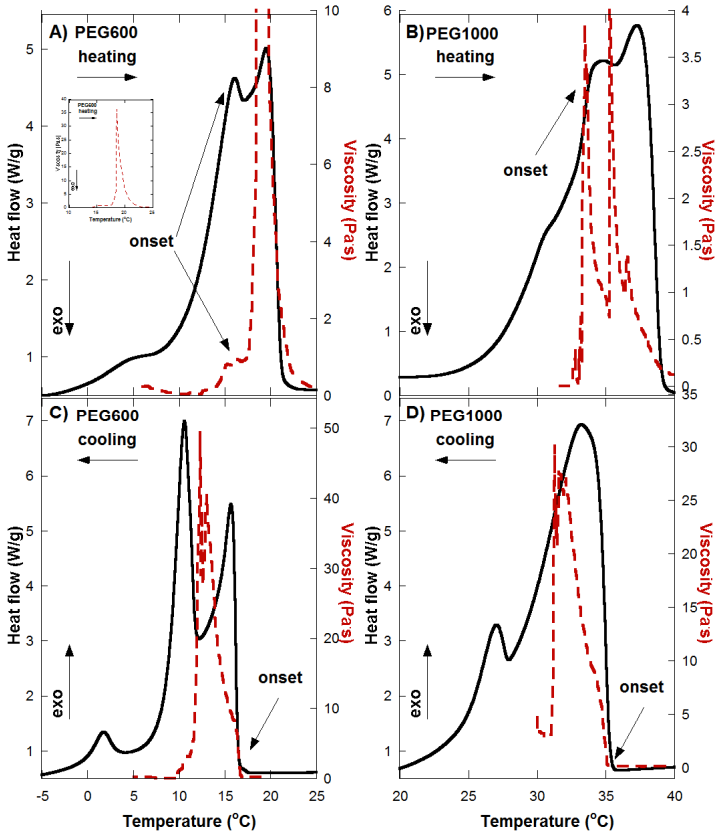

Figure 2. DSC and viscosity measurements for PEG600 (A and C) and PEG1000 (B and D).

Density Measurement Results

In Figure 3 the change in density for PEG600 (A) and PEG1000 (B) as a function of temperature during the solidification are compared to corresponding curves obtained by DSC on cooling. From the results it is obvious that the density increases when cooling the materials. There is also a drop in the density at the same temperature where the materials becomes solidified, i.e. at the temperature with the maximum heat flow in the DSC curves. The Anton-Paar density meter is not intended to be used on solid materials which could explain the sudden drop in density after it has reached its maximum value.

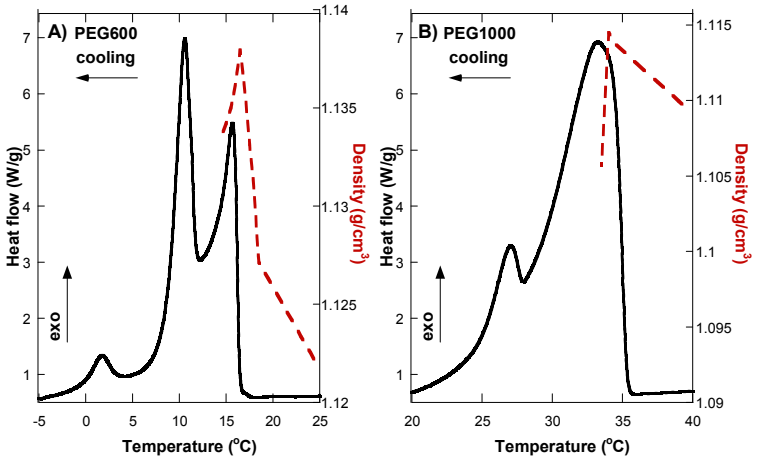

Figure 3. Comparison between DSC and density measurements for PEG600 (A) and PEG1000 (B).

Light Transmittance Measurement Results

Also the light transmittance shows a drop when the materials starts to solidify, i.e. when going from high temperatures to lower ones, as shown in Figure 4 for PEG1000 (A), PEG1500 (B), PEG4000 (C) and PEG6000 (D). Each material was evaluated in three subsequent measurements, each shown by the different curves (red, blue and green) in Figure 4. As can be observed, the rather abrupt drop in light transmittance is in well agreement with the peak maximum obtained by DSC. Further lowering of the temperature results in a larger part of the material becomes in its solid state, and consequently more opaque. At the temperature at which the material can be considered as completely solidified, the illuminance becomes close to zero, i.e. the materials are completely opaque due to the developed crystalline structure.

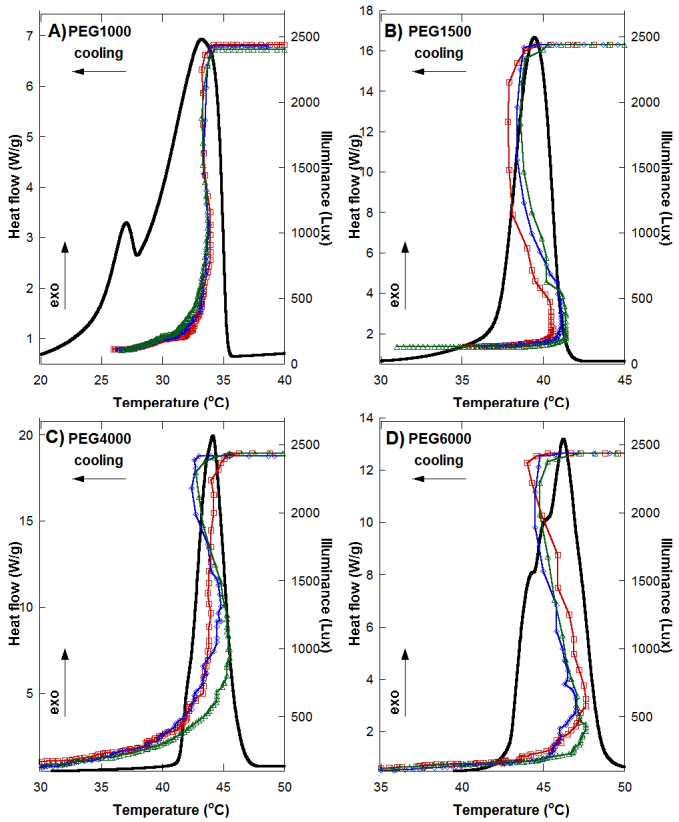

Figure 4. Comparison of the light transmittance of the material and the DSC measurements for PEG1000 (A), PEG1500 (B), PEG4000 (C) and PEG6000 (D). The red curve shows the first run, the blue curve shows the second run and the green curve shows the third run.

DISCUSSIONS

For PEG based PCMs it is possible to detect the liquid to solid transitions by changes in various physical properties such as viscosity, density and light transmittance, with a rather high accuracy, as shown in Figures 2-4. In this initial study the aim was to find ways for visualizing phase transitions for pedagogical reasons. For the solid to liquid like transition it was possible to identify the physical changes, but the reliability of the methods are uncertain due to instrumental limitations.

It was shown in Figure 2 that the onset of the viscosity changes are more consistent with the phase transition characteristics obtained by DSC when cooling compared to when the material is heated. In fact there is a perfect match between the onset of increase in viscosity and the start of phase transition (2B and D) on cooling. Worth noting is that the onset occurs at

different temperatures for the different PEGs dependent on their molecular weight (chain length). On heating (Figures 2A and C), on the other hand, the changes in heat flow clearly exceeds that of the onset of viscosity. This imply that it is easier to detect small changes in viscosity when the polymer chains become less movable, i.e. during the solidification, than if the chains become more movable in the melting process. However, as can be observed in Figure 2, heating does not induce sharp changes in heat flow (DSC data) similar to the case when cooling. The viscosity was assumed to reach a maximum value as the material reached complete solidification and then remain on that value during continued cooling. It was found that an air-gap could be seen between the rotating bob and the inner walls of the cup. As the bob rotates it pushes the solid material upwards over the bob. This explains the sudden drop in viscosity that occurs after solidification as well as the formation of different peaks during melting. As the material begins to melt, contact between the bob and the material interface results in a melting peak. Other measurement equipment with the ability to measure on solid materials could be further explored

The material had to be injected by a syringe into the machine in the density measurements. Therefore, it had to be melted prior to the experiment. The machine could only operate in a temperature range of approximately –20 °C to 90 °C and it was sensitive to corrosive materials. Those restrictions excluded measurements on other PCMs such as sugar alcohols and salt hydrates due to their high melting temperature and their corrosiveness, respectively. The density of the polymer was expected to increase during solidification, as expected (Eliassi et al., 1998), with a continuous increase when lowering the temperature. The method is normally used to measure the density of liquids and gasses and not solid materials. At the temperature at which the heat flow reaches its maximum, and the materials can be considered as a solid, there is a drop in the density. This explains the decline in density after the peak observed during solidification. The results show that the method is useful to identify when the solidification temperature is reached.

For the light transmittance measurements, the PCM has to be transparent in either its solid or liquid like phase. The PEGs showed this behavior and therefore the method is useful for this type of PCMs. For other types of PCMs further testing is required.

CONCLUSIONS

In this study three measurement techniques were applied on PEG based PCM during melting and solidification. Changes in viscosity, density and light transmittance were analyzed and compared to temperature curves for the phase transitions by DSC. The viscosity measurements showed good agreement with the DSC curves for the cooling curve. During heating the onset for the viscosity change was delayed compared to the DSC curve. The density and light transmittance were only measured during cooling but showed good agreement with the DSC results. This preliminary research study showed that although there are challenges for practical use of all three methods, they can be used as a foundation for development of technologies for visualizing phase transition.

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